Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 2012, **22**, 310–311
Mendeleev Communications

An unusual entangled motif based on a V-shaped imidazolyl ligand: 1D + 2D → 3D polycatenation

Jin-Song Hu,* Xi-Hui Liu, Jian-Jun Shi and Jie He*

School of Chemical Engineering, Anhui University of Science and Technology, Huainan 232001, P. R. China.
Fax: + 86 0554 666 8497; e-mail: jshu@aust.edu.cn

DOI: 10.1016/j.mencom.2012.11.010

The new polymer $[Cu(BIDPE)_2Cl_2][Cu(BIDPE)Cl_2]\cdot nH_2O$ has been prepared, and an X-ray diffraction study has revealed a $1D_{chain} + 2D_{sheet} \rightarrow 3D_{polycatenation}$ framework for this complex.

Entangled systems such as interpenetrated, polycatenated, polythreaded, and other species are a unique subset of supramolecular chemistry.[1–4] Intense interest in entangled systems is rapidly increasing due to not only their intriguing aesthetic structures but also potential applications in sorption,[5,6] heterogeneous catalysis[7,8] and photochemical areas.[9,10] Recently, more and more N-donor ligands have been widely employed to construct coordination polymers with fascinating architectures and interesting properties.[11–13] 4,4′-Bis(imidazol-1-yl)diphenyl ether (BIDPE), a V-shaped imidazolyl ligand, can be regarded as a half-flexible ligand.[14] To test the ability of this ligand to give new architectures and topologies, we synthesized a fascinating entangled motif of $[Cu(BIDPE)_2Cl_2]$-$[Cu(BIDPE)Cl_2]\cdot H_2O$ **1** based on BIDPE and $CuCl_2$.† Compound **1** represents an unusual $1D_{chain} + 2D_{sheet} \rightarrow 3D_{polycatenation}$ framework.

X-ray crystallography analysis‡ reveals that a crystal of **1** is made up of two kinds of species: a 1D zigzag chain and a 1D double-strand chain. The asymmetric unit contains two independent Cu^{II} cations, four Cl^- anions, three BIDPE ligands and one latticed water molecule. There are two types of coordination environments around Cu^{II} ions in the crystal structure. Figure 1 shows that Cu(2) has a trigonal coordination environment with two N atoms and one Cl^- anion; this configuration is relatively rare in Cu^{II} polymers. The Cu(1) centre is tetracoordinated to four N atoms from four BIDPE to form a square-planar geometry.

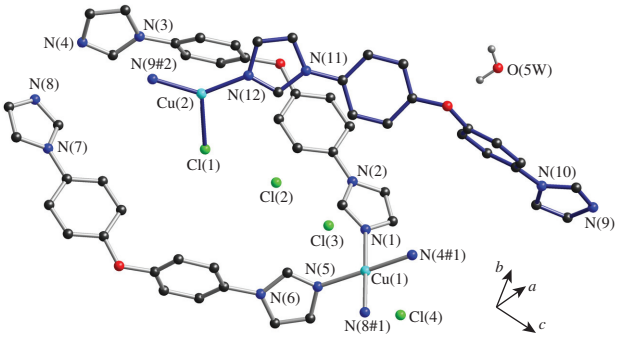

Figure 1 Coordination environment of **1**. The hydrogen atoms are omitted for clarity. Symmetry codes: #1 = *x*, *y*, 1 + *z*; #2 = –1 + *x*, *y*, –1 + *z*. Selected bond lengths (Å) and angles (°): Cu(1)–N(4#1) 1.997(3), Cu(1)–N(5) 2.003(3), Cu(1)–N(1) 2.010(3), Cu(1)–N(8#1) 2.020(3), Cu(2)–N(9#2) 1.938(4), Cu(2)–N(12) 1.939, Cu(2)–Cl(1) 2.3511(16); N(4#1)–Cu(1)–N(5) 176.96(15), N(4#1)–Cu(1)–N(1) 88.76(14), N(5)–Cu(1)–N(1) 92.76(13), N(4#1)–Cu(1)–N(8#1) 91.59(13), N(5)–Cu(1)–N(8#1) 86.86(13), N(1)–Cu(1)–N(8#1) 179.26(14), N(9#2)–Cu(2)–N(12) 140.75(16), N(9#2)–Cu(2)–Cl(1) 109.17(12), N(12)–Cu(2)–Cl(1) 109.57(12).

The neighbouring Cu(1) ions are linked by BIDPE to form an infinitely 1D double-strand chain, which contains a 32-membered $[Cu(1)_2(BIDPE)_2]$ metallocyclic ring, the adjacent distance of Cu(1)···Cu(1) is 15.419 Å. Cu(2) ions connected BIDPE and Cl^- to form an infinitely 1D zigzag chain; these two types of chains are arranged alternately (Figure 2). Further inspection shows that the coordinated Cl^- anions, the lattice water molecule and O_{centre} atoms of BIDPE from adjacent identical chains are actually contacting each other by H-bonding [donor···acceptor: O(5W)···O(3), 3.017 Å; O(5W)···Cl(1), 3.183 Å] (Figure 3).

Interestingly, the 1D double-strand chains are traversed by the Cl(1)···H(5A)–O(5W)–H(5B)···O(3) chains from 2D sheets to generate a new $1D_{chains} + 2D_{sheet} \rightarrow 3D_{polycatenation}$ framework.

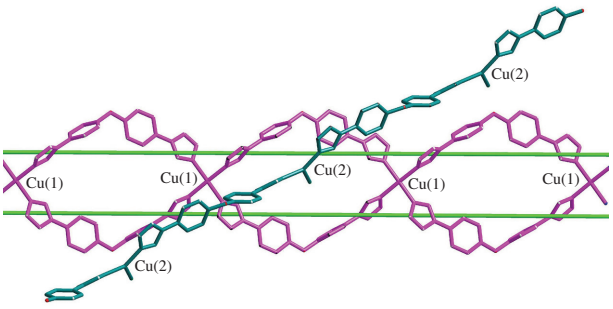

Figure 2 1D double-strand and zigzag chains arranged alternately.

† Crystal **1** was prepared by a solvothermal reaction: a mixture of $CuCl_2$ (0.15 mmol) and BIDPE (0.1 mmol) was dissolved in 8 ml of DMF/H_2O (1:1, v/v). The final mixture was placed in a Teflon-lined stainless steel Parr vessel (15 ml) and heated at 100 °C for 3 days; blue blank crystals were obtained (yield, 72% based on BIDPE).

‡ *Crystallographic data for* **1**: $C_{54}H_{44}Cl_4Cu_2N_{12}O_4$, M = 1193.91, monoclinic, space group $P2_1$, at 293 K: a = 8.8567(7), b = 18.4590(15) and c = 15.4191(12) Å, β = 90.509(2)°, V = 2520.7(3) Å^3, Z = 2, d_{calc} = = 1.573 g cm^{-3}, μ(MoKα) = 1.118 mm^{-1}, F(000) = 1220. 12 660 reflections were measured and 7875 independent reflections (R_{int} = 0.0260) were used in a further refinement. The refinement converged to wR_2 = = 0.1040 and GOF = 1.020 for all independent reflections [R_1 = 0.0419 was calculated against F for 7181 observed reflections with $I > 2\sigma(I)$]. The measurements were made on a Bruker Apex Smart CCD diffractometer with graphite-monochromated MoKα radiation (λ = 0.71073 Å). The structure was solved by direct methods, and the non-hydrogen atoms were located from the trial structure and then refined anisotropically with SHELXTL using full-matrix least-squares procedures based on F^2 values.[15] Hydrogen atom positions were fixed geometrically at calculated distances and allowed to ride on the parent atoms.

CCDC 907785 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2012.

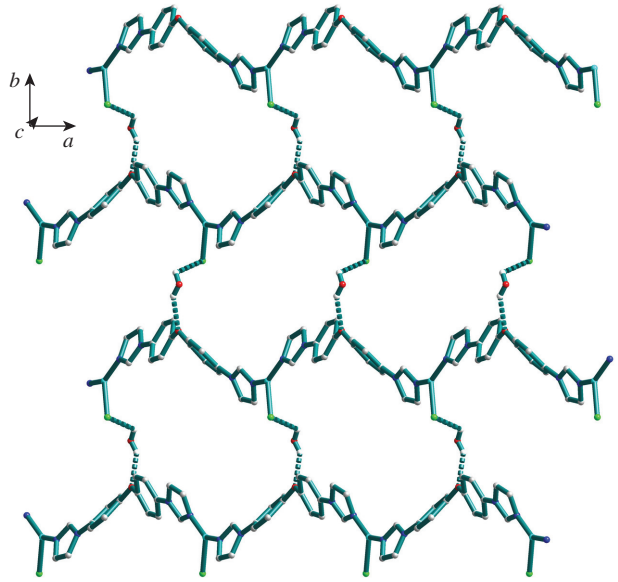

Figure 3 View of a 2D sheet constructed by zigzag chains and latticed water molecules.

In this framework, the interactions of Cl···Cl were observed, the distances [Cl(1)···Cl(2), 3.119 Å and Cl(2)···Cl(3), 3.106 Å] were shorter than the sum of van der Waals radii (3.520 Å).[16] The distances of Cu···Cl(3) and Cu–Cl(4) are 3.018 and 2.894 Å, respectively, also indicating the existence of weak interactions. These H-bonding, Cl···Cl and Cu···Cl interactions increase the stability of the framework (Figure 4). So far, a few 1D + 2D → 3D polycatenation coordination polymers were reported, one fascinating example of 1D + 2D → 3D polycatenation framework,

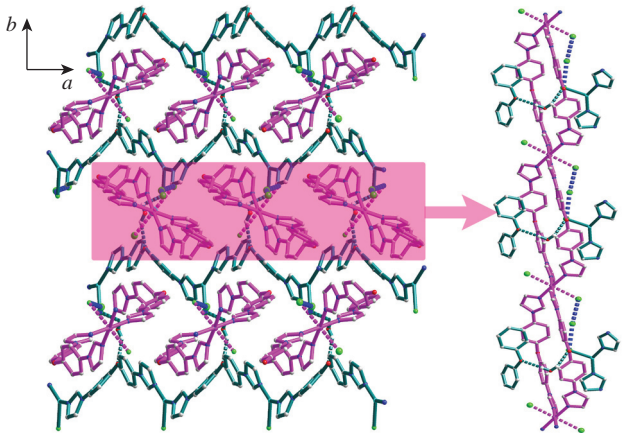

Figure 4 $1D_{chain} + 2D_{sheet} \rightarrow 3D_{polycatenation}$ framework.

$[Cu_5(bpp)_8(SO_4)_4(EtOH)(H_2O)_5](SO_4)\cdot EtOH\cdot 25.5H_2O$ [bpp = = 1,3-bis(4-pyridyl)propane], has been documented.[17] In that reported, the 2D sheet was generated by bpp and Cu^{II}. However, in **1**, the sheet was constructed by H-bonding. The results demonstrate that the latticed water can be well used as the structure-directing tool and can produce various H-bonding in the synthesis of unusual coordination frameworks.

This work was supported by the Natural Science Foundation of China (grant no. 21071004), the Start-up and Young Teacher's Research Foundation of Anhui University of Science and Technology (11227, 2012QNZ08) and the research fund of Key Laboratory for Advanced Technology in Environmental Protection of Jiangsu Province (AE201107).

References

1 J. Yang, J. F. Ma, S. R. Batten and Z. M. Su, *Chem. Commun.*, 2008, 2233.
2 X. H. Bu, M. L. Tong, H. C. Chang, S. Kitagawa and S. R. Batten, *Angew. Chem. Int. Ed.*, 2004, **43**, 192.
3 M. H. Zeng, W. X. Zhang, X. Z. Sun and X. M. Chen, *Angew. Chem. Int. Ed.*, 2005, **44**, 3079.
4 L. Carlucci, G. Ciani and D. M. Proserpio, *Coord. Chem. Rev.*, 2003, **246**, 247.
5 U. Eberle, M. Felderhoff and F. Schüth, *Angew. Chem. Int. Ed.*, 2009, **48**, 6608.
6 M. D. Allendorf, C. A. Bauer, R. K. Bhaktaa and R. J. T. Houka, *Chem. Soc. Rev.*, 2009, **38**, 1330.
7 A. Corma, H. García and F. X. Llabrés i Xamena, *Chem. Rev.*, 2010, **110**, 4606.
8 M. H. Xie, X. L. Yang and C. D. Wu, *Chem. Commun.*, 2011, **47**, 5521.
9 Z. Z. Lu, R. Zhang, Y. Z. Li, Z. J. Guo and H. G. Zheng, *J. Am. Chem. Soc.*, 2011, **133**, 4172.
10 A. G. Wong-Foy, A. J. Matzger and O. M. Yaghi, *J. Am. Chem. Soc.*, 2006, **128**, 3494.
11 M. J. Zaworotko, *Chem. Commun.*, 2000, 1.
12 S. A. Barnett and N. R. Champness, *Coord. Chem. Rev.*, 2003, **246**, 145.
13 J. S. Hu, Y. J. Shang, X. Q. Yao, L. Qin, Y. Z. Li, Z. J. Guo, H. G. Zheng and Z. L. Xue, *Cryst. Growth Des.*, 2010, **10**, 4135.
14 J. S. Hu, L. F. Huang, X. Q. Yao, Y. Z. Li, Z. J. Guo, H. G. Zheng and Z. L. Xue, *Inorg. Chem.*, 2011, **50**, 2404.
15 Bruker 2000, SMART (Version 5.0), SAINT-plus (Version 6), SHELXTL (Version 6.1), and SADABS (Version 2.03), Bruker AXS Inc., Madison, WI.
16 Y. Kobayashi, J. Maeda, T. Ando and K. Saigo, *Cryst. Growth Des.*, 2010, **10**, 685.
17 L. Carlucci, G. Ciani, M. Moret, D. M. Proserpio and S. Rizzato, *Angew. Chem. Int. Ed.*, 2000, **39**, 1506.

Received: 8th June 2012; Com. 12/3941